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I, Koichi ASANO of c/o Eiritsu Patent & Law Agency, Watase Bldg., 5-8, Nishi-Shimbashi 3-chome, Minato-ku, Tokyo hereby declare:

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1. That I am well acquainted with the Japanese and English languages:
2. That to the best of my knowledge and belief the document annexed hereto is a true English translation made by me of Japanese Patent Application No. 10-342308 in the name of former, Nippon Oil Co., Ltd., now, Nippon Mitsubishi Oil Corporation, which priority is claimed by European patent application No. 99970110.5.
3. Signed at Tokyo, Japan this 13th day of September, 2002.

Koichi ASANO

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【List of Documents】

【Name】 Specification 1 copy

【Name】 Document containing chemical formulae and the like 1 copy

【Name】 Abstract 1 copy

【General Power of Attorney No.】 9723863

[Designation of Document] SPECIFICATION

[TITLE OF THE INVENTION] GASOLINE COMPOSITION FOR DIRECT INJECTION GASOLINE ENGINE

[Claims]

[Claim 1] A gasoline composition for a direct injection gasoline engine comprising a polybutenyl amine composition.

[Detailed Description of the Invention]

[Technical Field to which the Invention Pertains]

This invention relates to gasoline compositions and more particularly to gasoline compositions having excellent detergency in combustion chambers particularly of direct injection gasoline engines.

[Description of the Prior Art]

From the view point of resource-savings and suppression of global warming, it has been a world-wide demand that the use of fossil fuels be reduced. In connection with this, an improvement in fuel consumption becomes the most important issue for gasoline-engine automobiles. On the other hand, some urban areas fail to meet environmental standards in terms of the amount of pollutants such as NO<sub>x</sub> (nitrogen oxide), and gasoline-engine automobiles are thus required to have reduced emissions of such pollutants. Direct injection gasoline engines are now considered to be the most effective means for meeting or satisfying such demands or standards.

Conventional gasoline engines are designed to form a homogeneous pre-mixture of gasoline and air by injecting gasoline into the intake port. In contrast, direct injection gasoline engines are designed to inject gasoline directly into the combustion chamber, so that they are able to form a stratified fuel mixture which is rich in the vicinity of the spark plug but highly lean elsewhere in the combustion chamber. Owing to the formation of such a stratified fuel

mixture, combustion with the highly lean mixture can be achieved, leading to an improvement in fuel consumption equivalent to that of diesel engines.

Moreover, the direct injection of gasoline into the combustion chamber is contributive to the freedom from delay in gasoline vaporization as seen in conventional engines, and enables further enhanced accuracy in control of fuel injection rate.

#### [Problems to be Solved by the Invention]

However, direct injection gasoline engines can encounter some unexpected problems which are different from those of conventional engines due to the direct injection of gasoline into the combustion chamber. One of the problems is related to deposits formed in the combustion chamber, particularly the cavity or recess formed on the upper surface of the pistons. The stratified combustion characterizing the direct injection gasoline engine is conducted by injecting fuel into the cavity while the piston is in upward stroke, and forming a rich fuel mixture in the vicinity of the spark plug with the rebounded fuel. If deposits are formed in the cavity during combustion, the ratio of air to fuel becomes unstable because a portion of the injected fuel is absorbed by the deposits. As a result, the amount of fuel around the spark plug is decreased, and the piston is delayed in reaching the top position of the cycle. Therefore, this problem causes an adverse affect on the drivability of automobiles, the deterioration of the exhaust gas, and the generation of smoke.

In view of the current situations, the present invention is intended to provide a gasoline additive which comprises a special nitrogen-containing compound having an excellent detergency in the combustion chamber, particularly in a recess or cavity formed on the upper surface of the piston of a direct injection gasoline chamber.

#### [Means for Solving the Problems]

After intensive research efforts made to solve the foregoing problems, it is found that nitrogen-containing compounds having specific structures are superior in detergency in a combustion chamber, particularly in cavities or recesses formed on the upper surface of the pistons of a direct injection gasoline engine.

That is, fuel composition according to the present invention are those comprising a polybutenyl compound.

[Mode for Carrying out the invention]

The present invention will be described in more detail below.

The other gasoline additive according to the present invention is a polybutenylamine compound. This compound may be those obtained by modifying the terminals of a polybutene compound obtained by polymerizing at least one member selected from n-butene, 2-butene and isobutene with an amine.

The second nitrogen-containing compound of the present invention is a polybutenylamine compound obtained by modifying the terminal ends of a polybutene compound derived from the polymerization of at least one member selected from n-butene, 2-butene and isobutene.

The polymerized portion constituting the polybutenylamine compound according to the present invention may be a homopolymer or copolymer of one or more members selected from n-butene, 2-butene and isobutene. The copolymer may be a random-, alternating- or block copolymer.

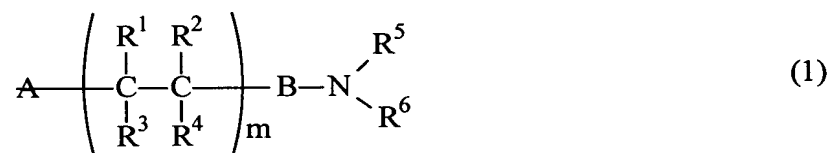
Eligible starting materials of the inventive polybutenylamine compound include n-butene, 2-butene and isobutene. Preferred is isobutene, because it provides a gasoline additive with enhanced detergency.

Although the polymerized portion of the polybutenylamine compound according to the present invention is formed by polymerizing a starting material

such as n-butene, 2-butene and isobutene, there may be other olefins present such as ethylene and propylene, in the starting material of the reaction.

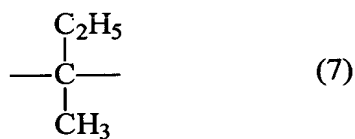
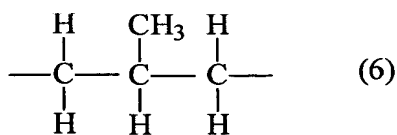
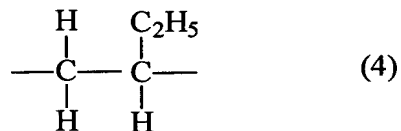
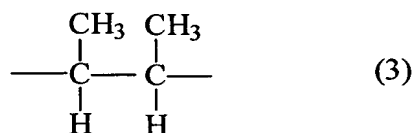
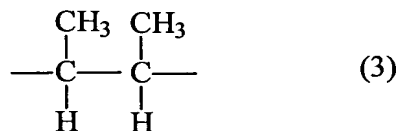
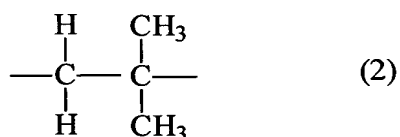
The polybutenylamine compound may have any of a hydrogen atom, a hydrocarbon group, an oxygen-containing group such as alkanol, and a nitrogen-containing group such as aminoalkyl, bonded to the nitrogen atom of the amine group.

The specific examples of the polybutenyl amine compound of the present invention are those represented by the formula

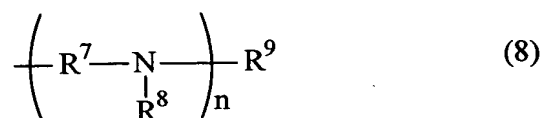


wherein A is n-butyl, sec-butyl or tert-butyl group,  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  are each independently a hydrogen atom, a methyl group, or an ethyl group, and are selected such that the total carbon number of  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  is 2, B is a group represented by formulae (2) to (7) below,  $R^5$  and  $R^6$  are each independently a hydrogen atom, a hydrocarbon group having 1 to 10 carbon atoms, an alkanol group having 1 to 8 carbon atoms or a group represented by formula (8) below and m is an integer of 1 to 100.

Formulae (2) to (7) are represented by



Formula (8) is represented by



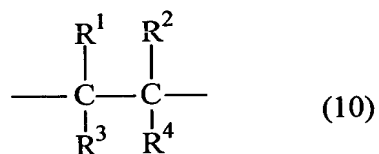
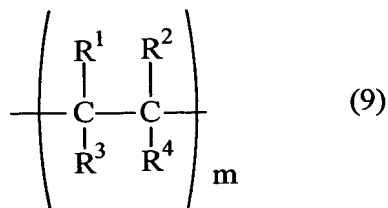
wherein  $\text{R}^7$  is an alkylene group having 1 to 4 carbon atoms,  $\text{R}^8$  is either a hydrogen or an alkyl group having 1 to 4 carbon atoms,  $\text{R}^9$  is either a hydrogen or a hydrocarbon group having 1 to 10 carbon atoms, and  $n$  is an integer of 1 to 5.

In formula (1), A can be any of n-butyl, sec-butyl or tert-butyl group, but is preferably tert-butyl, since tert-butyl provides an additive with an enhanced detergency.

$\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^3$  and  $\text{R}^4$  are each independently a hydrogen, a methyl or an ethyl group, selected such that the total number of carbon atoms in groups  $\text{R}^1 - \text{R}^4$  is always 2.

In the present invention, it is preferred that either  $\text{R}^1$  and  $\text{R}^3$  are each hydrogen when  $\text{R}^2$  and  $\text{R}^4$  are each a methyl group, or  $\text{R}^1$  and  $\text{R}^3$  are each a methyl group when  $\text{R}^2$  and  $\text{R}^4$  are each hydrogen.

The group of formula (9) below indicates the polymerization chain of the polybutenyl amine compound of formula (1) having a structural unit represented by formula (10) below:



wherein  $R^1$ ,  $R^2$ ,  $R^3$ ,  $R^4$ , and  $m$  are the same as those defined in formula (1).

The groups of formula (10) whose number is represented by “ $m$ ” in formulae (9) and (10) may be the same or different. They may be in the form of a homopolymer or a copolymer. Such a copolymer may be random- or alternating.

In formula (1),  $B$  is a group represented by one of formula (2) to (7), but is preferably the group of formula (2) or (6), more preferably the group of formula (6).

$R^5$  and  $R^6$  in formula (1) are each independently a hydrogen atom, a  $C_1 - C_{10}$  hydrocarbon group, a  $C_1 - C_8$  alkanol group or a group of formula (8) above.

The  $C_1 - C_{10}$  hydrocarbon group here encompasses  $C_1 - C_{10}$  straight or branched alkyl groups,  $C_2 - C_{10}$  straight or branched alkenyl,  $C_5 - C_{10}$  cycloalkyl or alkylcycloalkyl groups,  $C_6 - C_{10}$  aryl or alkylaryl groups and  $C_7 - C_{10}$  arylalkyl groups.

Specific examples of the  $C_1 - C_{10}$  alkyl group are methyl, ethyl, n-propyl, isobutyl, n-butyl, isobutyl, sec-butyl, tert-butyl, straight or branched pentyl, straight or branched hexyl, straight or branched heptyl, straight or branched octyl, straight or branched nonyl and straight or branched decyl groups.

Specific examples of the  $C_2 - C_{10}$  alkenyl group are ethenyl, n-propenyl, isopropenyl, n-butenyl, isobutenyl, sec-butenyl, tert-butenyl, straight or branched pentenyl, straight or branched hexenyl, straight or branched heptenyl, straight or branched octenyl, straight or branched nonenyl and straight or branched decenyl groups.

Specific examples of the  $C_5 - C_{10}$  cycloalkyl or alkylcycloalkyl group are cyclopentyl, cyclohexyl, cycloheptyl, methylcyclopentyl, dimethylcyclopentyl (inclusive of all positional isomers), ethylcyclopentyl (inclusive of all positional



isomers), straight or branched propylcyclopentyl (inclusive of all positional isomers), ethylmethylcyclopentyl (inclusive of all positional isomers), trimethylcyclopentyl (inclusive of all positional isomers), diethylcyclopentyl (inclusive of all positional isomers), ethyldimethylcyclopentyl (inclusive of all positional isomers), straight or branched propylmethylcyclopentyl (inclusive of all positional isomers), straight or branched propylethylcyclopentyl (inclusive of all positional isomers), methylcyclohexyl (inclusive of all positional isomers), dimethylcyclohexyl (inclusive of all positional isomers), ethylcyclohexyl (inclusive of all positional isomers), straight or branched propylcyclohexyl (inclusive of all positional isomers), ethylmethylcyclohexyl (inclusive of all positional isomers), trimethylcyclohexyl (inclusive of all positional isomers), diethylcyclohexyl (inclusive of all positional isomers), ethyldimethylcyclohexyl (inclusive of all positional isomers), straight or branched propylmethylcyclohexyl (inclusive of all positional isomers), methylcycloheptyl (inclusive of all positional isomers), dimethylcycloheptyl (inclusive of all positional isomers), ethylcycloheptyl (inclusive of all positional isomers), straight or branched propylcycloheptyl (inclusive of all positional isomers), ethylmethylcycloheptyl (inclusive of all positional isomers) and trimethylcycloheptyl groups (inclusive of all positional isomers).

Specific examples of the  $C_6 - C_{10}$  aryl or alkylaryl group are phenyl, tolyl, (inclusive of all positional isomers), xylyl (inclusive of all positional isomers), ethylphenyl (inclusive of all positional isomers), straight or branched propylphenyl (inclusive of all positional isomers), ethylmethylphenyl (inclusive of all positional isomers), trimethylphenyl (inclusive of all positional isomers), straight or branched butylphenyl (inclusive of all positional isomers), straight or branched propylmethylphenyl (inclusive of all positional isomers), diethylphenyl (inclusive of all positional isomers), ethyldimethylphenyl (inclusive of all

positional isomers) and tetramethylphenyl groups.

Specific examples of the  $C_7 - C_{10}$  alkylaryl group are benzyl, methylbenzyl (inclusive of all positional isomers), dimethylbenzyl (inclusive of all positional isomers), phenethyl, methylphenethyl (inclusive of all positional isomers) and dimethylphenethyl groups (inclusive of all positional isomers).

Specific examples of the  $C_1 - C_{10}$  alkanol group are hydroxymethyl, hydroxyethyl, straight or branched hydroxypropyl, straight or branched hydroxybutyl, straight or branched pentyl, straight or branched hexyl, straight or branched hydroxyheptyl, straight or branched hydroxyoctyl, straight or branched hydroxynonyl and straight or branched hydroxydecyl groups.

$R^5$  and  $R^6$  may be the group of formula (8). In formula (8),  $R^7$  is a  $C_1 - C_4$  alkylene group, such as methylene, ethylene, propylene (1-methylethylene, 2-methylethylene), trimethylene, butylene (1-ethylethylene, 2-ethylethylene), 1,2-dimethylethylene, 2,2-dimethylethylene, 1-methyltrimethylene, 2-methyltrimethylene, 3-methyltrimethylene and tetramethylene. In view of providing the resulting additive with an excellent detergency,  $R^{32}$  is preferably a  $C_1 - C_3$  alkylene group, such as methylene, ethylene, propylene (1-methylethylene, 2-methylethylene) and trimethylene groups.

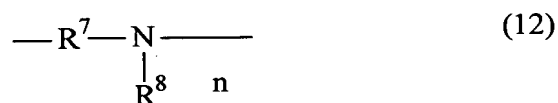
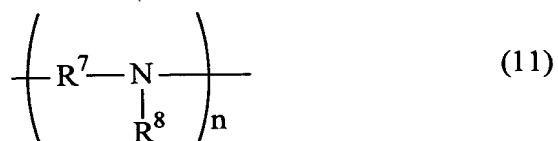
$R^8$  in formula (8) is hydrogen or a  $C_1 - C_4$  alkyl group. Specific examples of the  $C_1 - C_4$  alkyl group are methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl and tert-butyl. Among these, preferred for  $R^8$  are hydrogen and  $C_1 - C_3$  alkyl groups, more preferred are hydrogen, methyl and ethyl groups, and the most preferred is hydrogen.

$R^9$  in formula (8) is hydrogen or a  $C_1 - C_{10}$  hydrocarbon group. The  $C_1 - C_{10}$  hydrocarbon group here encompasses those already exemplified with respect to  $R^1$ .

Preferred for R<sup>9</sup> are hydrogen or C<sub>1</sub> – C<sub>3</sub> alkyl groups, more preferred are hydrogen, methyl and ethyl groups and the most preferred is hydrogen.

The letter, n, in formula (8) is an interger of 1 to 5, preferably from 1 to 3, more preferably 1 or 2, and most preferably 1.

The group of formula (11) contained in formula (11) has 1 to 5, preferably 1 to 3, more preferably 1 or 2, and most preferably 1 group of formula (12):



wherein R<sup>7</sup>, R<sup>8</sup>, and n are the same as those defined in formula (8).

Therefore, the group of formula (11) is a group obtained by the groups of formula bonded in the following manner:

- (1) bonding one type of groups of formula (12)
- (2) random-, alternating-, or block bonding the groups of formula (12).

"m" in formula (1) is an integer of 1 to 100. "m" is necessarily 1 or greater, preferably 5 or greater, and more preferably 10 or greater with the objective of the properties to retain dispersivity in a gasoline and detergency. "m" is necessarily 100 or less, preferably 50 or less, and more preferably 40 or less in view of bulb stick resulting from the increase of viscosity and influence on the deposit in the combustion chamber resulting from the deterioration of thermal decomposition.

The number-average molecular weight of a polybutenylamine compound of formula is not particularly restricted but is preferably 200 or greater, more preferably 400 or greater and even more preferably 700 or greater with the objective of dispersion properties and detergency in the gasoline. In order to

suppress valve-stick and the deterioration of thermal decomposition properties, leading to the formation deposits in a combustion chamber, caused by increased molecular weight, the number-average molecular weight of the polybutenylamine of formula (1) is preferably 6,000 or less, more preferably 3,000 or less, and further more preferably 2,400 or less.

The gasoline composition for use in a direct injection gasoline engine according to the present invention contains the above-described polybutenyl amine compound in an amount of 0.001 to 10 mass percent, based on the total mass of the composition. In order to enhance the detergency in the combustion chamber of a direct injection gasoline engine, particularly the cavity formed on the upper surface of the piston, the lower limit of the content of the nitrogen-containing compound is 0.001 mass percent, preferably 0.003 mass percent, more preferably 0.005 mass percent, even more preferably 0.01 mass percent, and most preferably 0.015 mass percent. No further enhancement effect can be expected at higher concentrations of additive. The upper limit of the additive content in a gasoline composition is 10 mass percent, preferably 5 mass percent, more preferably 4 mass percent, and most preferably 3 mass percent.

The base gasoline of the above-described gasoline composition may be prepared by blending various gasoline components.

Such components may be light naphtha derivable from atmospheric distillation of crude oil, cracked gasoline derivable from catalytic cracking or hydrocracking, reformed gasoline obtainable by catalytic reforming, polymerized gasoline obtainable by olefin polymerization, alkylates derivable from addition reaction or alkylation of a hydrocarbon such as isobutane with a lower olefin, isomerized gasoline derivable from conversion of light naphtha into isoparaffin using an isomerization device, de-n-paraffinized oil, butane, aromatic hydrocarbons and paraffinic fractions derivable from hydrocracking dimerized

propylene.

Shown below is a typical blend formulation of an unleaded gasoline which can be used in a direct injection gasoline engine by blending the nitrogen-containing compound according to the present invention.

- (1) reformed gasoline : 0 – 70 vol. %
- (2) light fractions of reformed gasoline  
(boiling at 25 – 120 °C) : 0 – 35 vol. %
- (3) heavy fractions of reformed gasoline  
(boiling at 110 – 200 °C) : 0 – 45 vol. %
- (4) cracked gasoline : 0 – 50 vol. %
- (5) light fractions of cracked gasoline  
(boiling at 25 – 90 °C) : 0 – 45 vol. %
- (6) heavy fractions of cracked gasoline  
(boiling at 90 – 200 °C) : 0 – 40 vol. %
- (7) alkylate : 0 – 40 vol. %
- (8) paraffin fraction derived from dimerization and subsequent  
hydrogenation of propylene : 0 – 30 vol. %
- (9) isomerized gasoline : 0 – 30 vol. %
- (10) MTBE : 0 – 15 vol. %
- (11) light naphtha : 0 – 2- vol. %
- (12) butane : 0 – 10 vol. %

If the benzene content of a gasoline compound needs to be reduced, the reformed gasoline may be added in less amount because it contains more benzene than the other gasoline components. Alternatively, the content of benzene may be reduced by using a reformed gasoline which is reduced in the benzene content by any suitable methods give below:

- (1) removing benzene fraction by distilling a reformed gasoline

- (2) extracting benzene from a reformed gasoline with a solvent such as sulforan
- (3) converting benzene into another compound by the following methods (A), (B) and (C),
  - (A) converting benzene by hydrogenating into cyclohexane, methylcyclohexane or the like,
  - (B) converting benzene by reacting it with C<sub>9</sub> or greater aromatic hydrocarbon into toluene, xylene, ethylbenzene or the like
  - (C) alkylating benzene with lower olefins such as ethylene and propylene or with lower alcohols such as methanol and ethanol,
- (4) using a reformer feed of desulfurization heavy naptha derived from removal of C<sub>6</sub> hydrocarbon by distillation, and
- (5) controlling the operation condition of a catalytic reforming apparatus.

Gasoline additives which can be used in combination with the nitrogen-containing compound according to the present invention include detergent dispersants such as succinimide and polyalkylamine; antioxidants such as phenol- or amine- ones; metal inactivating agents such as Schiff-type compounds and thioamide-type compounds; surface ignition preventers such as organophosphorus-derived compounds; antiicing agents such as polyalcohols and ethers thereof; combustion adjuvants such as alkali metal or alkaline earth metal salts of organic acids and sulfuric esters of higher alcohols; antistatic agents such as anionic surfactants, cationic surfactants and amphoteric surfactants; colorants such as azo dyes; rust inhibitors such as alkenyl succinate; identifying agents such as quinizarin and coumarin, and malodorants such as natural essential-based aromatics. One or more of these additives

may be blended in a gasoline composition in an amount which is preferably less than 0.1 mass percent, based on the total mass of the gasoline composition.

The gasoline composition comprising the inventive gasoline additive, other additives blended as required, and a base gasoline, will preferably exhibit the following distillation properties measured in accordance with JIS K 2254

“Petroleum products-Determination of distillation characteristics”

Running point at 10 vol. % ( $T_{10}$ ) : 35 – 55 °C

Running point at 30 vol. % ( $T_{30}$ ) : 55 – 75 °C

Running point at 50 vol. % ( $T_{50}$ ) : 75 – 100 °C

Running point at 70 vol. % ( $T_{70}$ ) : 100 – 130 °C

Running point at 90 vol. % ( $T_{90}$ ) : 120 – 160 °C

End point : 130 – 210 °C

The lower limit of ( $T_{10}$ ) is 35 °C, preferably 40 °C. A ( $T_{10}$ ) of lower than 30 °C would cause gasoline coking in an injector. The upper limit of ( $T_{10}$ ) is 55 °C, preferably 50 °C, more preferably 48 °C. A ( $T_{10}$ ) which is higher than 55 °C would lead to decreased low-temperature starting performance of an engine.

The lower limit of ( $T_{30}$ ) is 55 °C, preferably 60 °C. A ( $T_{30}$ ) of lower than 55 °C would invite objectionable high temperature engine performance and cause gasoline coking. The upper limit of ( $T_{30}$ ) is 75 °C, preferably 70 °C, and more preferably 68 °C. A ( $T_{30}$ ) which is higher than 75 °C would lead to aggravated low temperature engine performance.

The lower limit of ( $T_{50}$ ) is 75 °C, preferably 80 °C. A ( $T_{50}$ ) of lower than 75 °C would adversely affect low temperature engine performance. The upper limit of ( $T_{50}$ ) is 100 °C, preferably 95 °C, and more preferably 93 °C. A ( $T_{50}$ ) which is higher than 100 °C would adversely affect low- and normal-temperature engine performance.

The lower limit of ( $T_{70}$ ) is 100 °C, while the upper limit of ( $T_{70}$ ) is 130 °C, preferably 125 °C, more preferably 123 °C, and most preferably 120 °C. A ( $T_{70}$ ) which is higher than 130 °C would adversely affect low- and normal-temperature engine performance.

The lower limit of ( $T_{90}$ ) is 110 °C, preferably 120 °C. The upper limit of ( $T_{90}$ ) is 160 °C, preferably 150 °C, and more preferably 140 °C. A ( $T_{90}$ ) outside this range would affect low- and normal- temperature engine performance and cause an increase in emission of exhaust gas, the deterioration of engine oil, and the formation of sludge by reducing the level of engine oil diluted by gasoline.

The lower limit of the end point is preferably 130 °C, while the upper limit thereof is 210 °C, preferably 200 °C, more preferably 195 °C, and most preferably 190 °C. An end point which is higher than 210 °C would lead to poor engine performance at normal temperatures.

A gasoline composition containing an inventive gasoline additive should have a vapor pressure which is 70 kPa or less, preferably 65 kPa or less, more preferably 60 kPa or less, and most preferably 55kPa or less, in order to avoid the occurrence of coking and suppress the amount of evaporative emission. The term “vapor pressure” used herein denotes Reid vapor pressure (RVP) measured in accordance with JIS K 2258 “Testing Method for Vapor Pressure of Crude Oil and Petroleum Products (Reid Method)”.

The density of the gasoline composition containing the inventive gasoline additive should be within the range of 0.73 to 0.77 g/cm<sup>3</sup>. The lower limit of density is 0.73 g/cm<sup>3</sup>, preferably 0.735 g/cm<sup>3</sup>, as densities less than 0.73 would decrease fuel consumption efficiency. The upper limit of density is 0.77 g/cm<sup>3</sup>, preferably 0.76 g/cm<sup>3</sup>. Density in excess of 0.77 g/cm<sup>3</sup> would lead to insufficient acceleration and spark plug smoldering.



The density used herein denotes a density determined by JIS K 2451 "Testing Method for Densities of Crude Oil and Petroleum Products and Density-Mass-Volume Conversion Table".

The gasoline composition according to the present invention is substantially free of alkyl lead compounds such as tetraethyl lead. Even though the gasoline composition contains very small amount of such lead compounds, the amount thereof should be held below the lower threshold specified by JIS K 2255 "Petroleum products-Gasoline-Determination of lead content".

The gasoline composition according to the present invention should have a research octane number (RON) which is 89 or greater, preferably 90 or greater, more preferably 90.5 or greater, and most preferably 91 or greater. In order to enhance anti-knocking performance during high-speed driving, the inventive gasoline composition should have a motor octane number (MON) of 80 or greater, preferably 80.5 or greater, and most preferably 81 or greater.

Both RON and MON denote the values measured in accordance with JIS K 2280 "Petroleum products-Fuels-Determination of octane number, cetane number and calculation of cetane index".

The contents of paraffins, olefins and aromatics of the gasoline composition according to the present invention are preferably as follows:

Paraffins (V(P)) : 50 – 100 vol. %

Olefins (V(O)) : 0 – 15 vol. %

Aromatics (V(Ar)) : 0 – 35 vol. %

(V(P)) of the inventive gasoline composition should be in the range of 50 to 100 percent by volume, preferably 60 to 100 percent by volume, and more preferably 70 to 100 percent by volume with the objectives of precluding gasoline coking in an injector, reducing spark plug smoldering and ozone-generation ability of exhaust gas as well as the concentrates of benzene

contained therein and avoiding the generation of soot.

V(O) of the inventive gasoline composition should be 0 to 15 percent by volume, preferably 0 to 10 percent by volume, more preferably 0 to 7 percent by volume and most preferably 0 to 5 percent by volume with the objective of precluding gasoline coking in an injector.

V(Ar) of the inventive gasoline composition should be 0 to 35 percent by volume, preferably 0 to 30 percent by volume, more preferably 0 to 25 percent by volume and most preferably 0 to 20 percent by volume with the objective of precluding gasoline coking in an injector, reducing spark plug smoldering and ozone-formability of exhaust gas as well as the concentrates of benzene contained therein, and avoiding the generation of soot.

V(P), V(O) and V(Ar) are the values obtained by the measurement in accordance with JIS K 2536 "Liquid petroleum products-Testing method of components".

The inventive gasoline composition preferably meets the following conditions.

(1) V(Bz) : 0 – 1 vol. %

(2) V(Tol) : 0 – 30 vol. %

(3) V(C<sub>8</sub>A) : 0 – 20 vol. %

(4) V(C<sub>9</sub>A) : 0 – 5 vol. %

(5) V(C<sub>10</sub>+A) : 0 – 3 vol. %

(6) V(PA) = 0 or

when V(PA) ≠ 0, V(MA) / V(PA) : 1 or greater

(7) V(C<sub>4</sub>) : 0 – 10 vol. %

(8) V(C<sub>5</sub>) : 10 – 35 vol. %

(9) V(C<sub>6</sub>) : 10 – 30 vol. %

(10) V(C<sub>7</sub>+p) : 10 – 50 vol. %

(11)  $V(C_9+)$  : 0 – 10 vol. %

$V(Bz)$  denotes the amount of benzene, based on the total gasoline composition and should be in the range of 0 to 1 percent by volume, preferably 0 to 0.5 percent by volume. A  $V(Bz)$  which is 0 – 1 volume percent of benzene is contributive to a reduction in the concentration of benzene in the exhaust gas.

$V(Tol)$  and  $V(C_8A)$  denote the amount of toluene and the amount of a  $C_8$  aromatic hydrocarbon, respectively, based on the total gasoline composition.  $V(Tol)$  should be 0 to 30 percent by volume, preferably 0 to 20 percent by volume, while  $V(C_8A)$  should be 0 to 20 percent by volume, preferably 0 to 15 percent by volume. The  $C_8$  aromatic hydrocarbon may be either ethylbenzene or xylene (including all positional isomers).

$V(C_9A)$  denotes the amount of a  $C_9$  aromatic hydrocarbon, based on the total gasoline composition.  $V(C_9A)$  should be 0 to 5 percent by volume, preferably 0 to 3 percent by volume in order to lower the ozone generation ability by an exhaust gas. The  $C_9$  aromatic hydrocarbon may be n-propylbenzene, isopropylbenzene (cumene), ethylmethylbenzene (inclusive of all positional isomers) and trimethylbenzene (inclusive of all positional isomers).

$V(C_{10}+A)$  denotes the amount of an aromatic hydrocarbon having 10 or more carbon atoms, based on the total gasoline composition.  $V(C_{10}+A)$  should be 0 to 3 percent by volume, preferably 0 to 1 percent by volume, and more preferably 0 percent by volume in order to lower the ozone generating ability of exhaust gas. The aromatic hydrocarbon having 10 or more carbon atoms may be diethylbenzene (inclusive of all positional isomers), dimethylethylbenzene (inclusive of all positional isomers), tetramethylbenzene (inclusive of all positional isomers) and n-butylmethylbenzene (inclusive of all positional isomers).

$V(MA)$  and  $V(PA)$  denote the amount of an aromatic hydrocarbon having

one alkyl substituent (vol. %) and the amount of an aromatic hydrocarbon having more than two alkyl substituents (vol. %), respectively, based on the total gasoline composition. In the present invention, if  $V(\text{PA})$  is 0 or  $V(\text{MA})$  is not 0, the ratio of  $V(\text{MA})$  to  $V(\text{PA})$  should be held to 1 or greater, preferably 1.5 or greater, more preferably 2 or greater.

The above  $V(\text{Bz})$ ,  $V(\text{Tol})$ ,  $V(\text{C}_8\text{A})$ ,  $V(\text{C}_9\text{A})$ ,  $V(\text{C}_{10}+\text{A})$ ,  $V(\text{C}_9+)$ ,  $V(\text{MA})$  and  $V(\text{PA})$  are the values determined in accordance with JIS K 2536 "Liquid petroleum products-Testing method of components".

$V(\text{C}_4)$  denotes the amount of a  $\text{C}_4$  hydrocarbon, based on the total gasoline composition.  $V(\text{C}_4)$  is 0 to 10 percent by volume, preferably 0 to 5 percent by volume, and more preferably 0 to 3 percent by volume with the objective of further reducing the amount of evaporative emission. The  $\text{C}_4$  hydrocarbon may be any of n-butane, 2-methylbutane (isobutane), 1-butene, 2-butene and 2-methylpropene.

$V(\text{C}_5)$  denotes the amount of a  $\text{C}_5$  aliphatic hydrocarbon, based on the total gasoline composition. The lower limit of  $V(\text{C}_5)$  is 10 percent by volume, and preferably 15 percent by volume. The upper limit of  $V(\text{C}_5)$  is 35 percent by volume, and preferably 30 percent by volume. A concentration of 10 percent by volume or more of the  $\text{C}_5$  aliphatic hydrocarbon is contributive to the production of a gasoline composition which is capable of providing an excellent engine performance at normal temperature. A concentration of 35 percent by volume or less of the  $\text{C}_5$  aliphatic hydrocarbon is contributive to the production of a gasoline composition which is capable of providing an excellent engine performance at high temperature. With the objective of precluding gasoline coking in an injector, it is preferred that the unsaturated hydrocarbon content ( $V(\text{C}_5\text{O})$ ) in the  $\text{C}_5$  aliphatic hydrocarbon is 0 percent by volume, or that the ratio of the saturated hydrocarbon content to unsaturated hydrocarbon content

$(V(C_5P) / (V(C_5O))$ , should be 1 or greater, preferably 1.5 or greater, more preferably 2 or greater, and most preferably 3 or greater. The  $C_5$  saturated aliphatic hydrocarbon may be n-pentane, 2-methylbutane (isopentane) and 2,2-dimethylpropane (neopentane), while the  $C_5$  unsaturated aliphatic hydrocarbon may be 1-pentene, 2-pentene, 2-methyl-1-butene, 2-methyl-2-butene and 3-methyl-1-butene.

$V(C_6)$  denotes the amount of a  $C_6$  aliphatic acid hydrocarbon, based on the total gasoline composition. The lower limit of  $V(C_6)$  should be 10 percent by volume, preferably 15 percent by volume, while the upper limit of  $V(C_6)$  should be 30 percent by volume, preferably 25 percent by volume. A concentration of 10 percent by volume or greater of  $C_6$  aliphatic acid hydrocarbon is contributive to the production of a gasoline additive which is capable of providing an excellent normal temperature engine performance. A concentration of 30 percent by volume or less of  $C_6$  aliphatic acid hydrocarbon is contributive to the production of a gasoline additive which is capable of providing an excellent high temperature engine performance. With the objective of precluding gasoline coking in an injector, it is preferred that the unsaturated hydrocarbon content ( $V(C_6O)$ ) in the  $C_6$  aliphatic hydrocarbon should be 0 percent by volume, or that the ratio of the saturated hydrocarbon content to the unsaturated hydrocarbon content ( $V(C_6P) / (V(C_6O))$ , should be 2 or greater, preferably 3 or greater, more preferably 5 or greater, and most preferably 10 or greater.

Specific examples of the  $C_6$  saturated hydrocarbon are n-hexane, 2-methylpentane, 3-methylpentane, 2,2-dimethylbutane and 2,3-dimethylbutane. Specific examples of the  $C_6$  unsaturated hydrocarbon are 1-hexene, 2-hexene, 3-hexene, 2-methyl-1-pentene, 3-methyl-1-pentene, 4-methyl-1-pentene, 2-methyl-2-pentene, 3-methyl-2-pentene, 4-methyl-2-pentene, 2,3-dimethyl-1-butene, 3,3-dimethyl-1-butene and 2,3-dimethyl-2-butene.

$V(C_{7+P})$  denotes the amount of a saturated aliphatic hydrocarbon having 7 or more carbon atoms, based on the total gasoline composition. The lower limit of  $V(C_{7+P})$  should be 10 percent by volume, preferably 20 percent by volume, while the upper limit of  $V(C_{7+P})$  should be 50 percent by volume, and more preferably 45 percent by volume. A  $V(C_{7+P})$  which is 10 percent by volume or greater is contributive to the production of a gasoline composition providing an excellent normal temperature engine performance, while a  $V(C_{7+P})$  which is 50 percent by volume or less is contributive to the production of a gasoline composition providing an excellent high temperature engine performance. Specific examples of the saturated aliphatic hydrocarbon having 7 or more carbon atoms are n-heptane, 2-methylhexane, 3-methylhexane, 2,2-dimethylpentane, 2,3-dimethylpentane, 2,4-dimethylpentane, 3,3-dimethylpentane, 3-ethylpentane and 2,2,3-trimethylbutane.

$V(C_9+)$  denotes the amount of a hydrocarbon having 9 or more carbon atoms, based on the total gasoline composition.  $V(C_9+)$  should be in the range of 0 to 10 percent by volume, and preferably 0 to 5 percent by volume. A composition having a  $V(C_9+)$  in this preferred range will provide excellent low- and normal- temperature engine performance and will reduce the amount of gasoline which dilutes engine oil so as to preclude increased amounts of exhaust hydrocarbon, engine oil deterioration, and sludge formation.

The above  $V(C_4)$ ,  $V(C_5)$ ,  $V(C_5P)$ ,  $V(C_5O)$ ,  $V(C_6)$ ,  $V(C_6P)$ ,  $V(C_6O)$ ,  $V(C_{7+P})$  and  $V(C_{9+})$  are the values as determined by the following gas chromatography method. These values are measured using a methyl-silicone capillary column 25 to 50 mm in length, a helium or nitrogen carrier gas and an FID detector under the conditions of, 0.5 to 1.5 ml/min in gas flow rate, 1 : 50 to 1 : 250 in partition ratio, 150 to 250 °C in inlet temperature, - 10 to 10 °C in initial column temperature, 200 to 250 °C in end column temperature and 150 to 250 °C in

detector temperature.

The gasoline composition according to the present invention may contain oxygen-containing compound in such an amount that the mass percent of oxygen is 0 to 2.7, and preferably 0 to 2.0. The content of oxygen-containing compounds in excess of 2.7 mass percent would lead to an increase in fuel consumption and in NO<sub>x</sub> emission.

The nitrogen-containing compound described herein encompasses C<sub>2</sub> – C<sub>4</sub> alcohols and C<sub>4</sub> – C<sub>8</sub> ethers. Eligible nitrogen-containing compounds for the inventive gasoline composition include ethanol, methyl-tert-butylether (MTBE), ethyl-tert-butylether, tert-amylethylether (TAME) and tert-amylethylether, among which the preferred are MTBE and TAME, and the most preferred is MTBE. Methanol is not preferred because it is corrosive and would increase the concentration of aldehyde in exhaust gas.

The sulfur content of the inventive gasoline composition should be less than 50 mass ppm, preferably 30 mass ppm, more preferably 20 mass ppm, and most preferably 10 mass ppm. The sulfur content if greater than 50 mass ppm would result in poisoning of after-treatment catalysts, increases in the concentration of NO<sub>x</sub>, carbon monoxide, and hydrocarbons, and a sharp rise in benzene emission.

The term “sulfur content” used herein denotes the sulfur content measured in accordance with JIS K 2541 “Crude oil and petroleum products-Determination of sulfur content”.

The unwashed existing gum of the inventive gasoline composition should be present in an amount of 20 mg/100ml or less, and the washed gum should be present in an amount of 3 mg/100 ml or less, and preferably 1 mg/100ml or less, as measured in accordance with JIS K2261 “Petroleum products-Motor gasoline and aviation fuels-Determination of existent gum-Jet

evaporation method". Deviations from these amounts would lead to the formation of deposits in the fuel-induction system and the occurrence of agglutination in the intake valve.

The gross caloric value of the inventive gasoline composition should be 35,000 J/g or more, preferably 40,000 J/g or more, more preferably 45,000 J/g or more as measured by JIS K 2279 "Crude petroleum and petroleum products-Determination and estimation of heat combustion".

The oxidation stability of the inventive gasoline composition should be over 480 minutes, preferably over 1,440 minutes as measured in accordance with JIS K 2287 "Testing Method for Oxidation Stability of Gasoline (Induction Period Method)". Oxidation stability less than 480 minutes would lead to the formation of gum during storage of the composition.

The inventive gasoline composition should give a value of 1 or 1a in a copper corrosion test conducted at a temperature of 50 °C for 3 hours in accordance with JIS K 2513 "Petroleum products-Corrosiveness to copper-Copper strip test". Copper corrosion test values exceeding 1 would indicate that the composition is capable of causing the corrosion of pipes in a fuel system.

The kerosene content of the inventive gasoline composition should be within the range of 0 to 4 percent by volume, based on the total gasoline composition. The term "kerosene content" used herein denotes the content of  $C_{13} - C_{14}$  hydrocarbon (vol. %) based on the total gasoline composition, and is quantitatively determined by a gas chromatographic process in which a methyl-silicone caterpillar column having a column length of 25 to 50 m is fed with a helium or nitrogen gas at a flow rate of 0.5 to 1.5 ml/min. and a divisional ratio of 1 : 50 to 1 : 250 and is operated at an inlet temperature of 150 to 250 °C, an initial column temperature of - 10 to 10 °C, a final column temperature of 150 to



250 °C, and a hydrogen ion detector temperature of 150 to 250 °C.

Examples of the invention will now be provided, with the understanding that the invention is in no way limited by these examples.

First, a base gasoline used in Examples and Comparative Example was prepared by by mixing 60 parts by volume of catalytic reformed gasoline, 30 parts by volume of catalytic cracked gasoline and 10 parts by volume of alkylate. The properties of the resulting base gasoline are as follows:

Base gasoline properties

Reid vapor pressure : 0.65 kgf/cm<sup>2</sup>

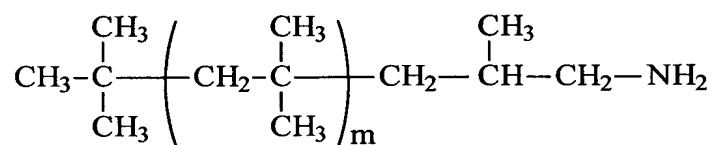
Specific gravity : 0.727

Boiling range : 30 – 190 °C

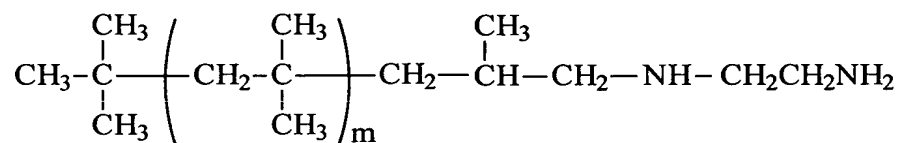
Octane number : 98.1

Gasoline compositions according to the present invention were prepared by blending the base gasoline with the following polybutenyl amine compounds in an amount shown in Table 1. The base gasoline alone was used for Comparative Example.

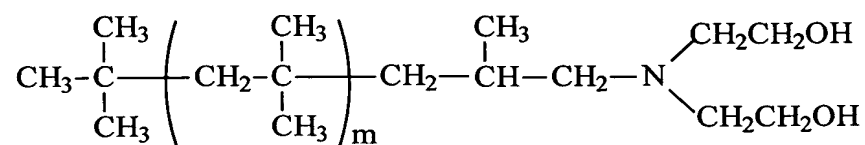
Compound 1: number-average molecular weight : 1,050



Compound 2: number-average molecular weight : 1,050



Compound 3: number-average molecular weight : 1,050



Each of the gasoline compositions were subjected to the following engine evaluating test. The results are shown in Table 1.

#### Engine Evaluating Test

A passenger car equipped with a 1.8-L displacement direct injection gasoline engine was used, and after repeating a 10.15 mode for 400 hours, exhaust gas was collected based on the 10.15 mode and the THC (Total Hydrocarbon) emission was measured. The engine was run at a constant speed of 40 km/h, and a 5-fold volume of exhaust gas was collected with a Bosch Smoke Meter to measure the smoke volume, after which the engine was disassembled to measure the amount of combustion chamber deposits.

Table 1

	Composition (mass %)		Engine Evaluation Test Results				
	Base Gasoline	Nitrogen-Containing Compound	Deposits (mg)			THC (g /km)	Smoke (%)
			Cavity (inside)	Cavity (outside)	Cylinder Head		
Example 9	[99.98]	Compound 9 [0.02]	158	583	854	0.12	4.8
Example 10	[99.98]	Compound 10 [0.02]	197	604	886	0.13	5.1
Example 11	[99.98]	Compound 11 [0.02]	202	615	870	0.13	5.2
Comparative Example 1	[100]	—	504	836	1282	0.18	10.4

As clearly shown by the engine evaluation test results in Table 1, the gasoline compositions of Examples 1 to 3 according to the invention were all capable of reducing combustion chamber deposits in direct injection gasoline engines. The reduction in deposits was particularly notable in the cavity directly which directly contacts fuel during stratified combustion. In addition, the increase in THC and smoke volume, believed to result from loss of control due to fuel adhesion by chamber deposits, was successfully inhibited.

[Designation of Document] ABSTRACT

[Abstract]

[Object] To provide a gasoline composition which is excellent in detergency of the combustion chamber of a direct injection gasoline engine.

[Constitution] A gasoline composition for a direct injection gasoline engine comprising a polybutenyl amine compound.